PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No.:	10/824,876
Filing Date:	April 15, 2004
Applicant:	Gregory P. Meisner et al.
Group Art Unit:	1754
Examiner:	Wayne A. Langel
Title:	IMIDE/AMIDE HYDROGEN STORAGE MATERIALS AND METHODS
Attorney Docket:	GP-302579 (8540R-000027/DVA)

DECLARATION OF PRIOR INVENTION IN THE UNITED STATES TO OVERCOME A CITED PUBLICATION PURSUANT TO 37 C.F.R. §1.131

PURPOSE OF DECLARATION

1. I am a co-inventor of the patent application identified above and inventor of the subject matter described and claimed therein, including of Claims 17-26, 28-34, and 36-51.

2. This declaration is being presented to establish conception and reduction to practice of the invention of the patent application identified above in the United States at a date prior to November 21, 2002.

FACTS & DOCUMENTARY EVIDENCE

3. Prior to November 21, 2002, having earlier conceived of the concept of a method of forming an imide hydrogen storage material by reacting a hydride and an amide, I submitted a record of invention to the legal department at General Motors Corporation. To establish the date of conception of the invention of the claims of this patent application, the attached record of invention document is submitted as Exhibit A. Exhibit A also contains portions of an internal presentation relating to and summarizing the record of invention, which was prepared and

presented before November 21, 2002. The redacted portions of Exhibit A either disclose dates that are all prior to November 21, 2002 or disclose personal confidential information. This document (hereinafter referred to as the "ROI") was: prepared prior to November 21, 2002; identifies me as a co-inventor; and discusses and illustrates our conceived invention.

4. Prior to November 21, 2002, our invention was reduced to practice and experiments were conducted to generate data detailed in Figures 1 and 2 of the above identified patent application and in the lab notebook pages describing experimental details regarding lithium imide systems (attached as Exhibit B). The detailed description of the above identified patent application (at Paragraphs 36-42) details how the data was generated to create Figures 1 and 2, respectively. To establish the date of reduction to practice of the subject matter as claimed in this patent application, Exhibit B contains laboratory test data illustrating reduction to practice prior to November 21, 2002. The redacted portions of Exhibit B are dates that are all prior to November 21, 2002.

DECLARATION

5. As the person signing below: I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURE

Dated: 4/4/07

Frederick E. Pinkerton

Frederick E. Pinkerton

EXHIBIT A

37 C.F.R. §1.131 Declaration of Frederick E. Pinkerton
U.S.S.N. 10/824,876 entitled "Imide/Amide Hydrogen Storage Materials and Methods."

GP-302579

INVENTION FILE OPENED

[redacted]

CLASS:

POSTPONED:

GP-302579

HYDROGEN STORAGE MEDIUM

Gregory P. Meisner
Frederick E. Pinkerton
Martin S. Meyer
Michael P. Balogh
Matthew D. Kundrat

R & D

Kathy Marra

302579 (BSQR Book)

Inter-Organization

GM

Research & Development and Planning

Date: [redacted]

Subj: R&D and Planning Record of Invention File No. GP-302578

To: Kathryn A. Marra
GM Corporation Legal Staff
300 Renaissance Center
M.C. 482-C23-B21
P.O. Box 300
Detroit, MI 48265-3000

Attached is the Record of Invention entitled "Hydrogen Storage Medium" in the name(s) of Gregory P. Meisner (430), Frederick E. Pinkerton (430), Martin S. Meyer (430), Michael P. Balogh (460), and Matthew D. Kundrat (A).

Carol E. Siino
Intellectual Property Coordinator
M.C. 480-106-359
810/986-2520

Attachment

C: Materials & Processes (430)
Chemical & Environmental Sciences (460)
Aerotek (A)

CONFIDENTIAL AND PRIVILEGED

GENERAL MOTORS CORPORATION

File No. GP-302579

RECORD OF INVENTION

This Record of Invention must be completed with sufficient detail so that your invention can be understood and evaluated by both your engineering management and by a GM Legal Staff patent attorney. Novelty and competitive significance of your invention will be evaluated based on the information you provide.

Invention Title: Hydrogen Storage Medium

Inventor #1

Name: Gregory (First Name) P. (Middle Initial) Meisner (Last Name) Citizen of: USA

Social Security No. [redacted] GM Employee: ☒ Yes ☐ No ☒ Salary ☐ Hourly ☐ Contract

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Non-GM Employer Address: (Street) (City and State) (Zip Code)

* If there are more than two (2) inventors for this invention use the template at the end of this form.

[redacted]

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RECORD OF INVENTION

This Record of Invention must be completed with sufficient detail so that your invention can be understood and evaluated by both your engineering management and by a GM Legal Staff patent attorney. Novelty and competitive significance of your invention will be evaluated based on the information you provide.

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Inventor #1

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* If there are more than two (2) inventors for this invention use the template at the end of this form.

[redacted]

File Number: GP-302579

Answer questions 1 - [redacted]ompleting all of them to the best of yo[redacted]nowledge.

1. This invention was first thought of on: [redacted]

2. This invention has been or is expected to be disclosed outside GM on: *N/A*

3. This invention has been used or is committed to be used in production on: *N/A*

4. This invention has been offered for sale outside GM on: *N/A*

5. Was this invention made while working on a Government Contract? ☐ Yes ☒ No

   If yes, identify the government Contract No. *N/A*

6. Identify the product or process in which the invention is incorporated: *Hydrogen storage, Fuel Cells*

7. List all individuals who can provide information about the making of the invention. This list may include individuals who made the first sketch, description, or tests and individuals who are familiar with the facts relating to the making of the invention.
   Gregory P. Meisner, Frederick E. Pinkerton, Martin S. Meyer, Michael P. Balogh, Matthew D. Kundrat, Jan F. Herbst, Stephen J. Swarin, and Gary G. Tibbetts.

8. Each inventor has a legal duty to disclose all information known that is material to patentability of this invention. Such information includes the relevant prior art, which may be in the form of current or past products, equipment, processes, materials, patents, publications, advertisements, displays, and unpublished developments and proposals—whether originated by you, others in GM, competitors, suppliers, customers or others. Such information also includes disclosure of this invention outside GM, sales and offers of products using this invention, use of this invention in production and disputes about who should be considered as an inventor of this invention. To comply with the duty to disclose, list here and attach a copy of all such information, to the extent known.
   1.Robert Juza and Karl Opp, Z. anorg. Allg., 266, 313 (1951).
   2.Phin Chen, "Hydrogen Storage in Metal Nitride Systems", MRS Spring Meeting, V5.18 (2002).

Answer question 9 thoroughly.

9. Describe the invention in sufficient detail so that its nature, operation and usefulness can be understood. (Attach drawings, diagrams and further description, when necessary. Additional guidelines are listed below.)

This hydrogen storage medium is based upon the following general reversible chemical reaction:

$$2\,M^{x}(NH)_{x/2} + xH_2 \longleftrightarrow M^{x}(NH_2)_x + M^{x}H_x$$

where M is a metal or mixtures of metals(e.g. Li, Na, Mg, Ca, Al, Ti, Fe, Zn, etc.), x is the valence state of the metal or average valence state of the metal mixture, N is nitrogen, and H is hydrogen. The essential material is either the metal imide $[2M^{x}(NH)_{x/2}]$ or mixture of the metal amide and metal hydride $[M^{x}(NH_2)_x + M^{x}H_x]$. The absorption or desorption of hydrogen is determined/controlled by the temperature and hydrogen pressure of the storage medium.

We have demonstrated this hydrogen storage medium in the lithium system, $Li_3NH + H_2 \longleftrightarrow LiNH_2 + LiH$.

This system can be formed from a wide variety of starting materials and preparation techniques including but not limited to the following:

1. *Mixing an equal molar ratio of lithium amide ($LiNH_2$) and lithium hydride (LiH) according to the following reaction.*

   $$LiNH_2 + LiH \longleftrightarrow Li_2NH + H_2$$

   We have demonstrated this method in the laboratory. Mixing was accomplished using standard ball milling techniques.

2. *Reacting an equal molar ratio of lithium nitride (Li_3N) and lithium amide ($LiNH_2$) according to the following reaction:*

   $$Li_3N + LiNH_2 \longrightarrow 2Li_2NH$$

   We have demonstrated this method in the laboratory. Mixing was accomplished using standard ball milling techniques.

3. *Evolving ammonia from lithium amide ($LiNH_2$) according to the following reaction:*

   $$2LiNH_2 \longrightarrow Li_2NH + NH_3$$

   We have demonstrated this method in the laboratory.

4. *Hydriding lithium nitride (Li_3N) according to the following reaction:*

   $$Li_3N + 2H_2 \longrightarrow LiNH_2 + 2LiH$$

   This method has been demonstrated in the laboratory, but it produces excess lithium hydride which decreases the hydrogen storage capacity of the device.

The lithium system absorbs hydrogen at temperatures of ≥145°C and hydrogen pressures of ≥5-15KPa and desorbs at temperatures ≥125°C and hydrogen pressures ≤ 10KPa.

Mechanical and Electrical Devices: Include illustrations assigning reference numbers to the main elements and refer to the reference numbers in a description that explains how the main elements are connected or related and how they operate.

Electrical Circuits and Controls: Include circuit diagrams and a functional description.

Computer Software and Manufacturing or Business Processes: Include a flowchart or other step-by step overview.

Chemical Inventions: Identify all essential materials used, and alternatives therefor, in chemical terms – not tradenames. Identify and quantify all significant variables (e.g. temperature, pressure, concentration, pH etc.) of the process or material specifying operating ranges and the preferred example. Discuss the significance of each variable. Provide a recipe for at least one working example of the invention.

[redacted]

File Number: GP 3-2579

I hereby assign this invention to General Motors Corporation
and authorize General Motors Corporation to file an application on my behalf.

INVENTOR – SIGNATURE	GREGORY P. MEISNER (ALSO, PRINT NAME)	[redacted] DATE
INVENTOR – SIGNATURE	Frederick E. Pinkerton (ALSO, PRINT NAME)	[redacted] DATE
INVENTOR – SIGNATURE	Martin S. Meyer (ALSO, PRINT NAME)	[redacted] DATE
INVENTOR – SIGNATURE	Michael P. Balogh (ALSO, PRINT NAME)	[redacted] DATE
INVENTOR – SIGNATURE	Matthew D. Kundrat (ALSO, PRINT NAME)	[redacted] DATE

This invention was reviewed and understood by me:

1st WITNESS – SIGNATURE	Stephen J. Swarin (ALSO PRINT NAME)	[redacted] DATE
2nd WITNESS – SIGNATURE	Jan F. Herbst (ALSO, PRINT NAME)	[redacted] DATE

Answer the following questions if helpful in describing this Invention

10. What benefits will be realized by using this invention?

The benefit of this invention is a feasible hydrogen storage medium for automotive applications.

11. What is the state of development of this invention?

Reversible hydrogen storage has been successfully demonstrated in the lithium imide (Li_2NH), lithium amide ($LiNH_2$), and lithium hydride (LiH) system.

12. To the extent known, what alternatives exist for accomplishing substantially the same result as this invention?

Hydrogen can be stored either as a compressed gas, cryogenically cooled liquid, or in a solid. Solid hydrogen storage includes high surface area carbonaceous material, or hydrogen containing materials (e.g. MgH_2, Mg_2NiH_4, $LaNi_5H_6$, $NaAlH_4$, $NaBH_4$, $LiBH_4$, etc.). Current hydrogen storage systems lack capacity, have slow kinetics, have poor shelf life, require high or low temperatures, require high pressures, or are not reversible. Thus, they are not practical for automotive applications.

13. Describe the background of the invention. This description may include the state of the prior art and may identify deficiencies in the prior art that are overcome by this invention.

At the 2002 Materials Research Society (MRS) Spring Meeting, Ping Chen of the National University of Singapore presented her work on "HYDROGEN STORAGE IN METAL NITRIDE SYSTEMS". In this presentation, Ping Chen presented her work showing Lithium nitride (Li_3N) absorbs hydrogen forming lithium amide ($LiNH_2$) and lithium hydride (LiH), claiming that the reaction is reversible. Our work shows that the reaction is not reversible, but in fact desorbs hydrogen to form lithium imide (Li_2NH). Our work also shows that starting from lithium nitride results in excess lithium hydride, which does not contribute to reversible hydrogen storage. Therefore we have identified new synthesis routes that eliminate the excess lithium hydride.

Inventor # 3

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[redacted]

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[redacted] File Number: GP-302579

Inventor # 5

Name: Matthew (First Name) D. (Middle Initial) Kundrat (Last Name) Citizen of: USA

Social Security No. [redacted] GM Employee: ☐ Yes ☒ No ☐ Salary ☐ Hourly ☒ Contract

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LEGAL STAFF

[redacted] File Number: GP 302578

Hydrogen Storage Medium

GP-302579

Greg Meisner, Fred Pinkerton, Martin Meyer, Mike Balogh, Matt Kundrat

What is the Idea?

- Reversibly store H_2 using a metal imide
- The H_2 is released by heating the storage medium
- Four synthesis routes identified

Li-N-H Reactions

$$Li_3N \xrightarrow{+H_2} Li_2NH + LiH \xleftrightarrow{+H_2} LiNH_2 + 2LiH$$

Reversible H_2 storage capacity 5.2 wt%

$$2LiNH_2 \xrightarrow{-NH_3} Li_2NH \xleftrightarrow{+H_2} LiNH_2 + LiH$$

Reversible H_2 storage capacity 6.5 wt%

$$LiNH_2 + LiH \xleftrightarrow{-H_2} Li_2NH$$

Reversible H_2 storage capacity 6.5 wt%

$$Li_3N + LiNH_2 \longrightarrow 2Li_2NH \xleftrightarrow{+2H_2} 2LiNH_2 + 2LiH$$

Reversible H_2 storage capacity 6.5 wt%

(ROI: Meisner, Pinkerton, Meyer, Balogh, & Kundrat)

How does it work?

- H_2 reacts with the imide forming the hydride & amide:

$$2\ M^{+x}(NH)_{x/2} + xH_2 \longleftrightarrow M^{+x}(NH_2)_x + M^{+x}H_x$$

where M is Li, Na, Mg, etc… and x is the valence state.

- Heating releases the H_2 and reforms the imide.
- H_2 storage demonstrated in the lithium system:

$$Li_2NH + H_2 \longleftrightarrow LiNH_2 + LiH$$

(6.5wt% theoretical reversible capacity)

Prior art

- H_2 storage in lithium nitride previously reported*.

$$Li_3N + 2H_2 \longrightarrow LiNH_2 + 2LiH \ (\longleftrightarrow Li_2NH + LiH + H_2)$$

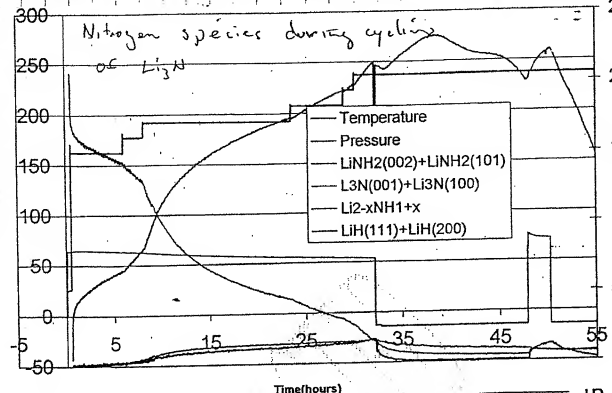
(5.2wt% theoretical reversible capacity)

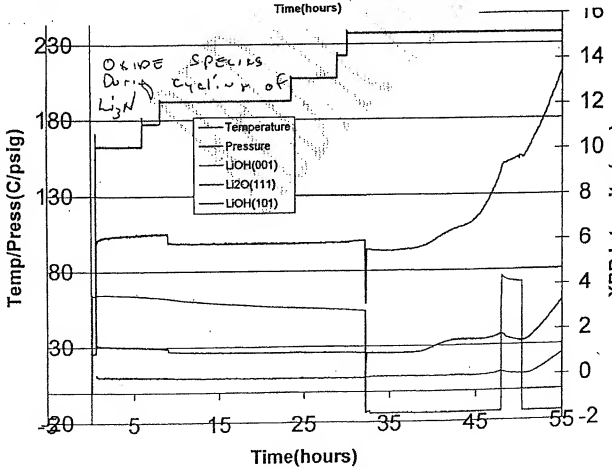
**Ping Chen, Materials Research Society Symposium Proceedings, v 730, V5.18, April 2002*

EXHIBIT B

37 C.F.R. §1.131 Declaration of Frederick E. Pinkerton
U.S.S.N. 10/824,876 entitled "Imide/Amide Hydrogen Storage Materials and Methods."

DATE [redacted]





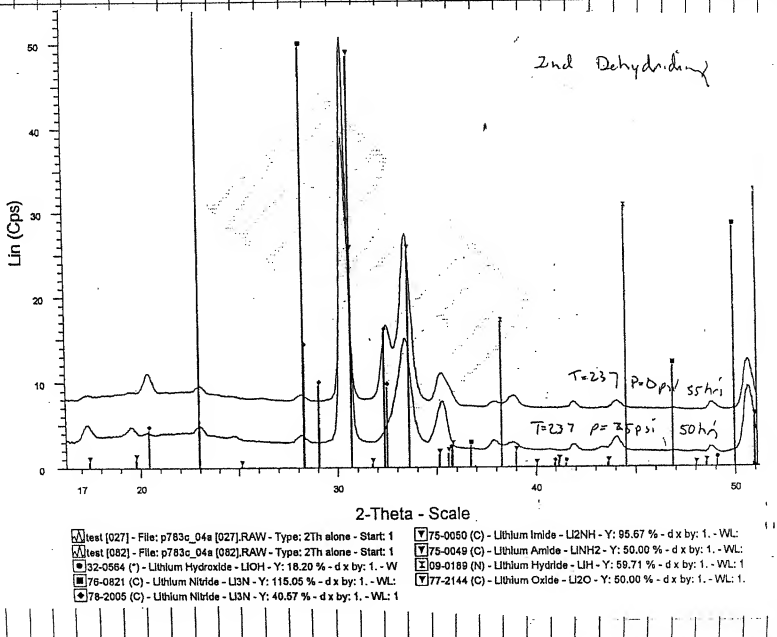
WITNESSED [redacted]

WITNESSED [redacted] SIGNATURE [redacted]

DATE 9-4

WITNESSED

SIGNATURE



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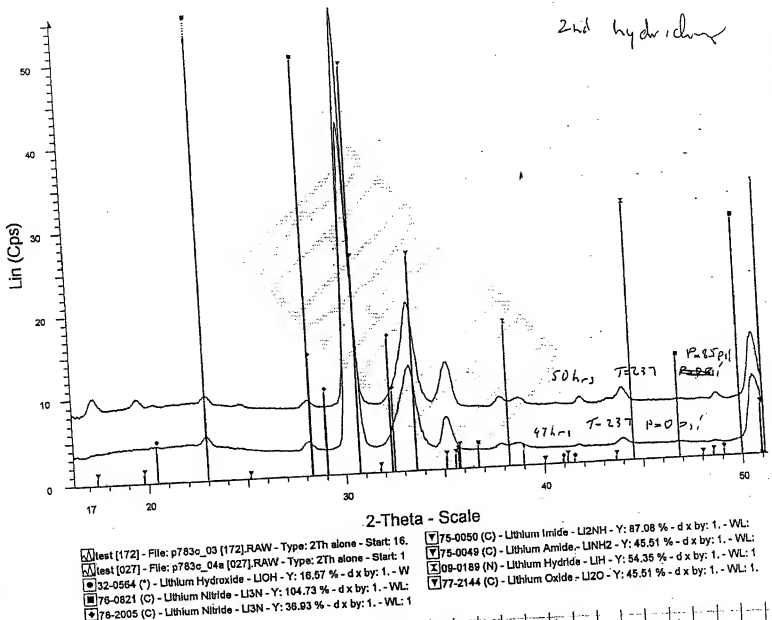

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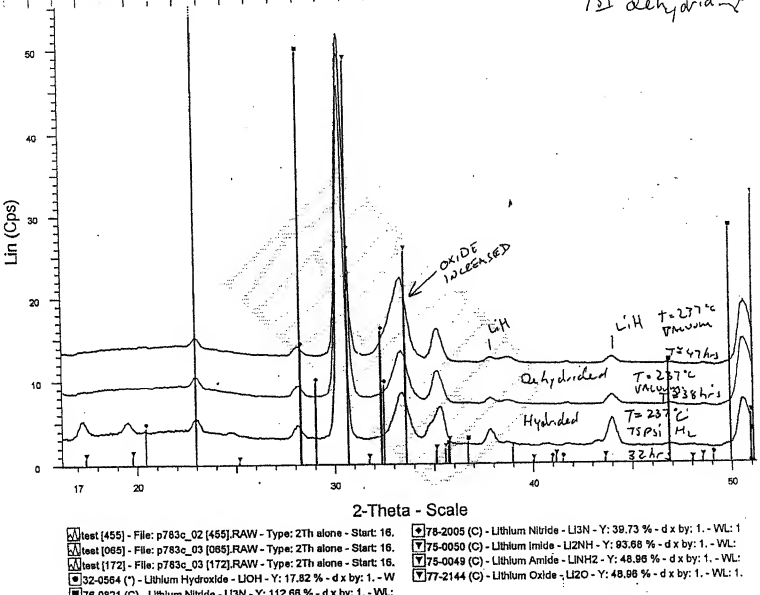
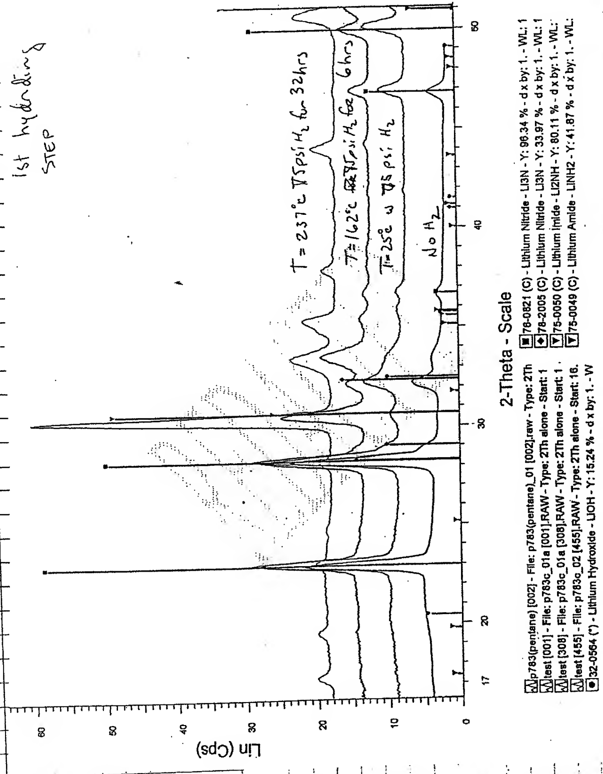


DATE [redacted]



WITNESSED [redacted]

WITNESSED

SIGNATURE

DATE [redacted] Thru [redacted]

Li3N Hydrogen Storage RxD

In situ XRD Li3N obtained from
F Pinkerton workshop Pentagon
XRD Files p783e-01_000.gfrm
" -01-475
" -02_000.gfrm
-02-454
03-000
03_163
04_000
04_082

Dayfab Files: Exp-0 MAN-013 ASC
MAN-014 ASC
15 ASC
16 ASC
17 ASC
18 ASC

Reaction from XRD Phase

Results
analysis

$$LiN_3 + 2H_2 \rightarrow LiNH_2 + 2LiH \longleftrightarrow Li_2NH + LiH + H_2$$

WITNESSED Frederick E. Pinkerton [redacted]

WITNESSED [redacted] SIGNATURE

[redacted] $P_m = 1537$ $T_s = 21.2$ end log file
$T_m = 26.9$ $T_F = 22°C$

Li_3N powder loaded

log file Li_3N_001_log 20 sec

Li_3N	9.955 (holder)
	10.700 sple+holder
	⇒ 0.745 g
	+ wool ~ 45 mg

heat to 150°C valves 5,6,7 open $T_{sp} = 170$

at 9:59am # 568 $T_s = 153.7$
$T_F = 156$
$T_{sp} = 170$

Run PCI : Small Holder #25

Li_3N Li3N 1st Run 156°C
400 T
* 100 slm ~~300 sec~~
8200 max p.
1.79 g/cc High Res
0.745 gms

ρ : estimated from
$LiNH_2$ $\rho = 1.178$

$\rho_{Li_3N} \cong (1.178) \frac{34.83 \text{ g/mole } Li_3N}{22.96 \text{ g/mole } LiH_2N}$

$= 1.79$ g/cc

$T_{sp} = 170°C$
$T_F = 157°C$
$T_s = 154.9°C$

[redacted] Run end @ 22:25 [redacted]

$x = 7.51$ 56.42 mg $T = 159.0°C$
not much desorption